Chemistry 17: Section Handout 2

Topics: *electronegativity; ionic, covalent, and polar covalent bonding; VSEPR theory; MO Theory; Hybridization and the MO Fragment Approach; FMO Theory (using orbitals to understand reactivity)*

Bonding

Electronegativity: the tendency of an atom or functional group to attract electrons towards itself.

-As the electronegativity of an atom or functional group increases, the electrons in its orbitals are held more tightly.

-As the electronegativity of an atom or functional group increases, its atomic orbitals become more stable (lower in energy).

H 2.1						
Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.6	Cl 3.0

increasing electronegativity

increasing electronegativity

* Note that H and C have *very* similar electronegativities. We will often treat them as being identical.

* Differences in electronegativity (ΔEN) define the type of bonding that occurs between two atoms.

Ionic bonds: bonds resulting purely from electrostatic interactions between a cation (positively charged) and an anion (negatively charged).

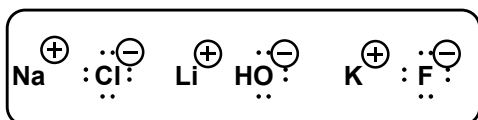-Valence electrons are localized entirely around the anion.

-Ionic bonds form when $\Delta EN > 2.0$, which is generally true for bonding between metals and non-metals.

Covalent bonds: bonds resulting from sharing elecrons between two nuclei (form when $\Delta EN \leq 2.0$).
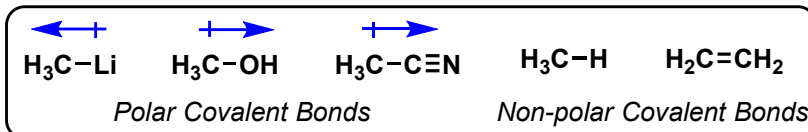
-*Nonpolar covalent bonds*: form when sharing of electrons is relatively equal ($\Delta EN < 0.5$).

-*Polar covalent bonds*: form when sharing of electrons is unequal, such that electron density is distorted towards the more electronegative atom ($0.5 \leq \Delta EN \leq 2.0$)).

Examples:

Ionic Bonds, EN > 2.0

Na⁺ :Cl:⁻   Li⁺ HO:⁻   K⁺ :F:⁻

Covalent Bonds, EN < 2.0

H_3C-Li H_3C-OH $H_3C-C\equiv N$ H_3C-H $H_2C=CH_2$

Polar Covalent Bonds   *Non-polar Covalent Bonds*

Valence Shell Electron Pair Repulsion Theory (VSEPR): a model used to predict the shape of individual molecules by assuming that electron pairs (bonds and lone pairs) repel each other to achieve the largest spacing that is geometrically possible. The geometry name describes the shape of the bonding domains.

| Steric Number (bonds + lone pairs)	Lone Pairs		
	0 lone pairs	*1 lone pair*	*2 lone pairs*
2	180° X−A−X *Linear (CO₂)*		
3	X−A⁗X 120° X *Trigonal Planar (BF₃)*	A X X *Bent (SO₂)*	Bond angles with lone pairs are more acute than with bonds
4	X 109.5° X−A⁗X X *Tetrahedral (CH₄)*	A X⁗X X *Trigonal Pyramidal (NH₃)*	A X X *Bent (H₂O)*

Molecular Orbital (MO) Theory:

Covalent bonds can be described as the combination of atomic orbitals (AOs) (s, p, sp^3, sp^2, sp, etc.) to form molecular orbitals (MOs). When two AOs overlap and combine, *two* new MOs are formed: an in-phase and an out-of-phase interaction.

- ***Bonding MO***: the orbital that results when AOs that are in-phase with each other combine. The bonding MO is lower in energy then the starting AOs.

- ***Antibonding MO***: the orbital that results when AOs that are out-of-phase with each other combine. The antibonding orbital is denoted with a * and is higher in energy then the starting AOs. Antibonding orbitals always contain a nodal plane (region of no electron density), and the phasing of the orbital changes across the node.

- ***Non-bonding MO***: the orbital that results when AOs cannot combine, and therefore remain unchanged. If occupied by a lone pair (non-bonding electrons), it is denoted n_Z (where Z = atom).

Interaction Energy =
$E = $ (orbital overlap) $/ (\varepsilon_A - \varepsilon_B)$
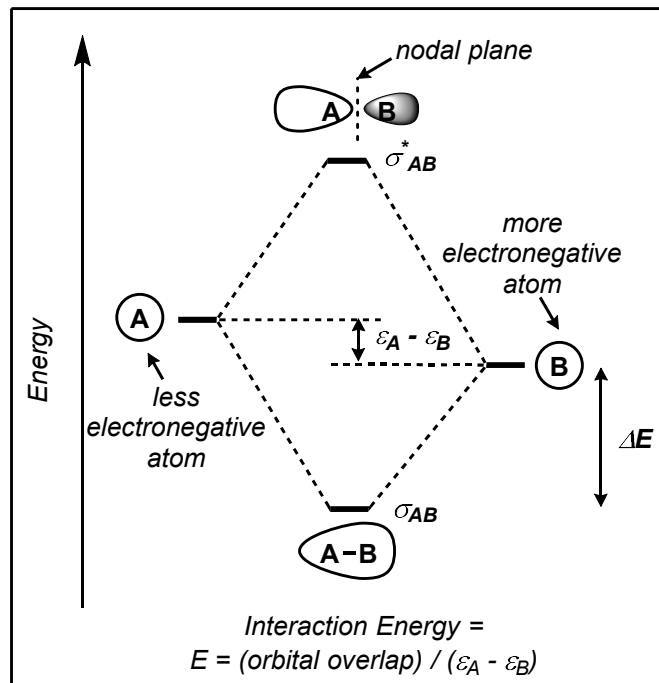
MO Types and Energies:

(1) Sigma bonds (σ) occur from head-on overlap between AOs. Pi bonds (π) occur from side-on overlap between p AOs.

(2) When an orbital interaction occurs between two different atoms, the interaction energy is dictated by:

- spatial overlap - how similar in shape in size the AOs are (and how well they can overlap in space)
- energetic overlap - how similar in energy the AOs are before they interact (determined by electronegativity)

(3) *The relative order of orbital energies can be predicted as follows: all σ < all π < all n < all π^* < all σ^**

(4) The relative ordering of energies within a bond type is difficult to predict. You can assume that within an orbital class (σ, π, n, π^*, σ^*), *orbitals with more electronegative atoms will be lower in energy*. For example: $\pi^*_{C-O} < \pi^*_{C-C}$, $n_O < n_N$, and $\pi_{C-O} < \pi_{C-C}$
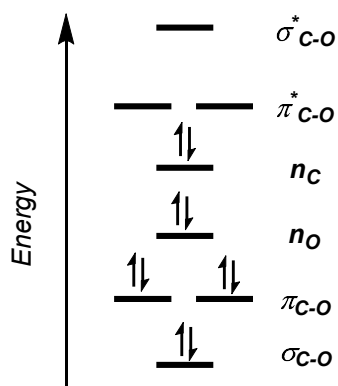
Example: $:C \equiv O$ ⊖ ⊕

Bonds and Lone Pairs:
1 $\sigma_{(C-O)}$ bond;
2 $\pi_{(C-O)}$ bonds;
1 lone pair on C;
1 lone pair on O

→

Molecular Orbitals
1 $\sigma_{(C-O)}$ and 1 $\sigma^*_{(C-O)}$ orbital;
2 $\pi_{(C-O)}$ and 2 $\pi^*_{(C-O)}$ orbitals;
1 nC orbital;
1 nO orbital

Shortcut for Providing MOs:

1) List locations of electrons in the molecule (bonds and lone pairs). Don't forget "hidden" H's

2) List the corresponding MOs.

2) Draw the MO diagram by ordering the MOs, using the guidelines listed above to determine their relative energies.

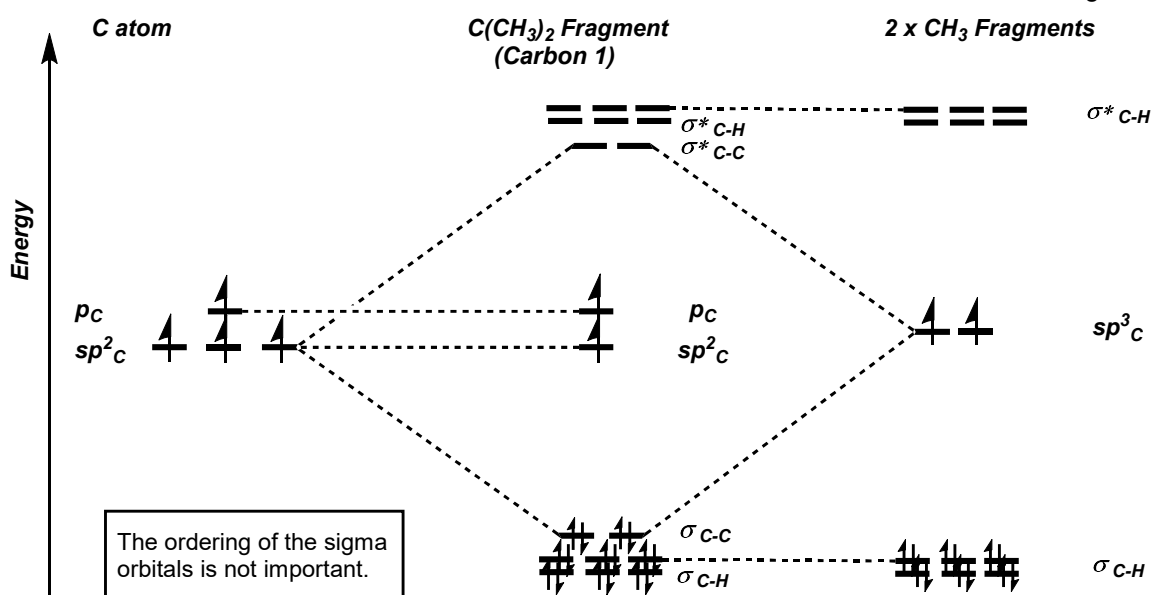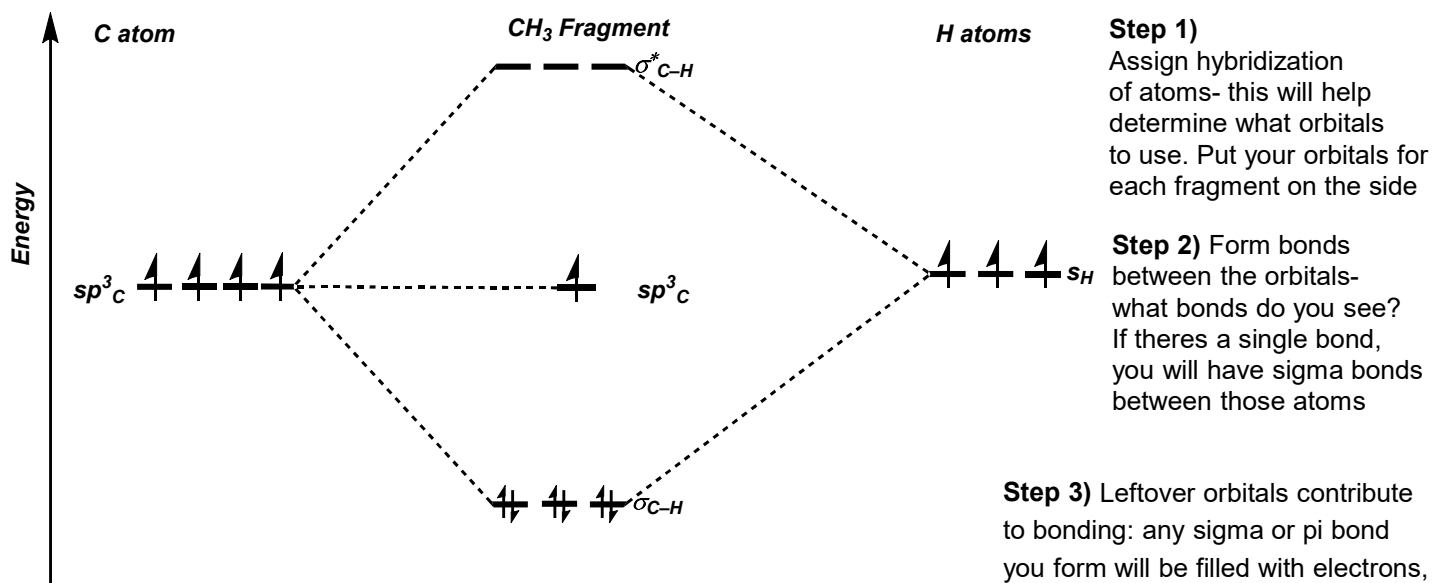3) Count the number of electrons present in the molecule and fill in the MO diagram accordingly.

Where do I put MOs when the atom is charged?

1) Positive charge lowers all MOs of a molecule (the molecule wants electrons more when it's positive, so it's harder to remove them)

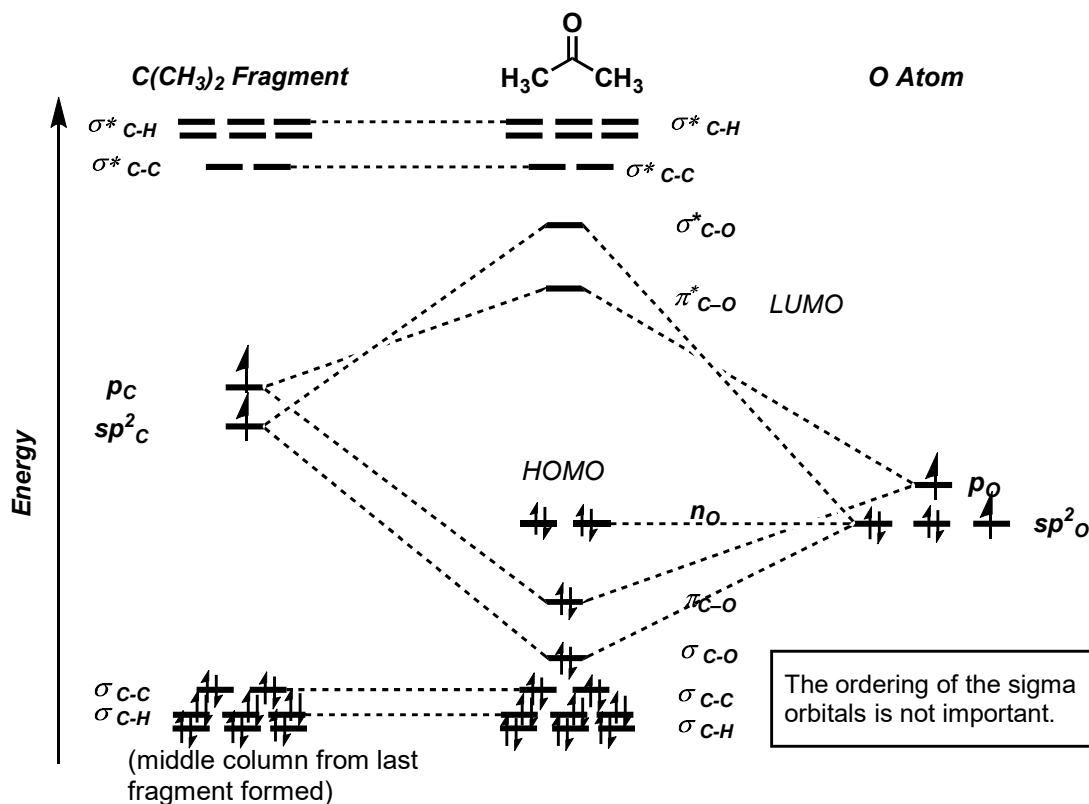2) Negative charge raises all MOs of a molecule (less electronegative when there's an excess of electrons)

Fragment MO Approach: A method for constructing MOs in which the MOs for pieces/fragments of the molecule are constructed independently, then brought together to build the MOs for the entire molecule. As the fragments are constructed, some, but not all, atomic orbitals are combined, resulting in molecular orbitals (for that fragment) and remaining unused atomic orbitals (for use in bringing all the fragments together).

O
H_3C
1
CH_3
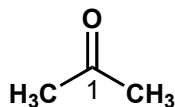
Fragment MO Construction example: To construct the MO diagram for acetone, approach each component. Construct MO diagrams of the $C(CH_3)_2$ fragment from their constituent C and H atomic orbitals and CH_3 fragment orbitals, and then add the oxygen (provided). Label all atomic and molecular orbitals, and place all orbitals at the appropriate relative energies.

Energy
C atom
CH_3 Fragment
H atoms
σ^*_{C-H}
sp^3_C
sp^3_C
s_H
σ_{C-H}

Step 1) Assign hybridization of atoms- this will help determine what orbitals to use. Put your orbitals for each fragment on the side

Step 2) Form bonds between the orbitals- what bonds do you see? If theres a single bond, you will have sigma bonds between those atoms

Step 3) Leftover orbitals contribute to bonding: any sigma or pi bond you form will be filled with electrons, but we have a leftover sp^3 orbital. These become our orbitals to bond with in our next step (use the middle column as your side columns in the next fragment)

Energy
C atom
$C(CH_3)_2$ Fragment (Carbon 1)
2 x CH_3 Fragments
σ^*_{C-H}
σ^*_{C-C}
σ^*_{C-H}
p_C
sp^2_C
p_C
sp^2_C
sp^3_C
σ_{C-C}
σ_{C-H}
σ_{C-H}

The ordering of the sigma orbitals is not important.

Step 4) We need our central carbon to bond with our methyl groups, so we use its lowest energy electrons (sp^2) to bond with the free orbitals of the methyls. This forms more sigma bonds

C(CH$_3$)$_2$ Fragment   **H$_3$C** O **CH$_3$**   **O Atom**

Energy (vertical axis)

σ^*_{C-H} ≡≡≡ --------- ≡≡≡ σ^*_{C-H}

σ^*_{C-C} ▬ ▬ --------- ▬ ▬ σ^*_{C-C}

σ^*_{C-O} ▬

π^*_{C-O} ▬   LUMO

p_C
$sp^2{}_C$

HOMO n_O p_O $sp^2{}_O$

π_{C-O}

σ_{C-O}

σ_{C-C} σ_{C-C}
σ_{C-H} σ_{C-H}

(middle column from last fragment formed)

> The ordering of the sigma orbitals is not important.

Step 5) Now we are adding an oxygen to our fragment, which is much more electronegative than carbon. When an atom is more electronegative or stabilized, we put the atomic orbitals lower in energy, which is why the oxygen orbitals are lower. Oxygen will have the same hybridization as the carbon because of their bonding. T*he sp^2 electrons can be used to form sigma bonds, but p orbital electrons must be used to form the pi bond(due to their geometry). This leaves extra sp^2, even though they are lower in energy than p. Geometry of your orbitals are key for bonding!*

We have leftover electrons that don't end up in bonds, and those represent our lone pairs on oxygen, which we would expect based off of the octet rule. At any point, double check your MO diagrams with your intuition on the bonding of your molecule.

To fill in the diagram with electrons, check your list of what bonds you have, and add a pair to each bond you see. Then add in lone pair electrons you expect. The highest energy pair of electrons are your HOMO, and the lowest empty orbital are your LUMO. Now you have an MO diagram of a complex molecule, you can use it to see how it reacts with other compounds!

Hybridization: the mixing of s and p AOs to form hybridized orbitals (sp^3, sp^2, or sp). Hybridized orbitals are localized on a single atom and simplify MO analysis because they have the directionality and energies needed to form bonds with the desired molecular geometry (tetrahedral, trigonal planar, or linear).
-Hybridized orbitals can be generated in the following manner:

$(s + p_x + p_y + p_z) = 4\ sp^3\ orbitals$

$(s + p_x + p_y) + p_z = 3\ sp^2\ orbitals\ + 1\ remaining\ p\ orbital$

$(s + p_x) + p_y + p_z = 2\ sp\ orbitals\ + 2\ remaining\ p\ orbitals$

Notice:
1) The total number of orbitals remains constant before and after hybridization.
2) Any p AOs that are not used to make hybridized orbitals remain as p AOs.

-The relative energies of AOs and hybrid AOs depends on the extent of p character. Orbitals with more p character are higher in energy because the electrons are further away from the nucleus and therefore less stabilized.

Relative energies of s, p, sp³, sp², and sp orbitals:

Spatial orientation of hybridized orbitals:

sp³	sp³	sp³	sp³
sp²	sp²	sp²	p
sp	sp	p	p
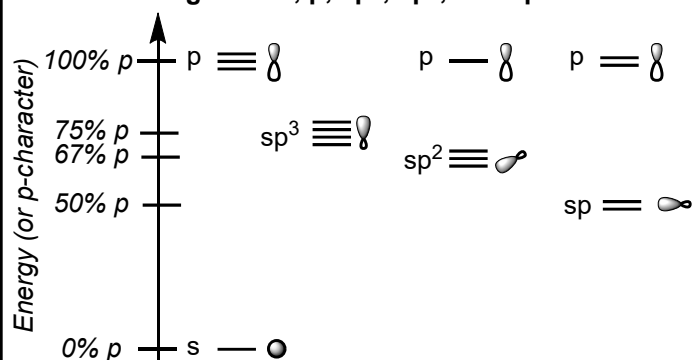
To determine the hybridization of an atom, count the number of electron domains (regions about an atom where there are electrons):
- four: sp³ (example: C in CH_4, N in NH_3)
- three: sp² + p (example: C & O in CH_2O)
- two: sp + 2p (example: C & N in HCN)

Examples: Using hybrid AOs with MO theory
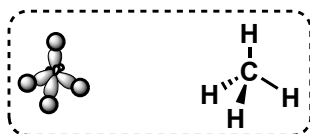
Methane
4 σ-bonds from
4 sp³ orbitals on C +
1 s orbital on each H

Ammonia
3 σ-bonds + 1 lp from
4 sp³ orbitals on N
1 s orbital on each H

Exceptions: If an atom with a **lone pair is next to a π bond, the atom will usually hybridize** so that the lone pair can occupy a p orbital in order to interact with the π bond through resonance. This is common in carbonyl-containing compounds and in molecules containing heteroatoms adjacent to aryl rings.
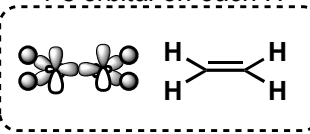
Ethylene
5 σ-bonds from
3 sp² orbitals on each C +
1 s orbital on each H and
1 π bond from 1 p orbital on each C
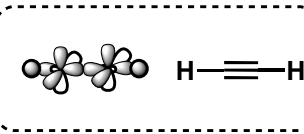
Acetylene
3 σ-bonds from
2 sp orbitals on each C +
1 s orbital on each H and 2
π bonds from 2 p orbitals on each C
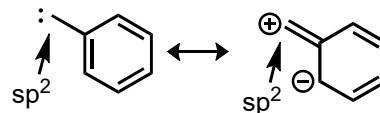
Frontier Molecular Orbital (FMO) Theory: a tool for predicting and explaining reactivity of organic molecules by describing reactions in terms of the interaction between the *frontier molecular orbitals* of the reactive partners.
The frontier molecular orbitals consist of:
(1) the highest-occupied molecular orbital (HOMO)
(2) the lowest-unoccupied molecular orbital (LUMO)

- For two reactive partners (A and B) in principle, two HOMO-LUMO interactions could occur: **(1)** $HOMO_A$–$LUMO_B$ or **(2)** $HOMO_B$–$LUMO_A$.

- The HOMO–LUMO interaction with the *smaller energy difference* between the two orbitals (greater energetic orbital overlap) will dictate how the two partners react. These reacting partners will be called the nucleophile-electrophile pair.

Nucleophile: Neutral or negatively charged reactive partners that act as electron donors. Nucleophiles react with the electrons in their HOMO, and better nucleophiles have higher-energy HOMOs.

Electrophile: Neutral or positively charged reactive partners that act as electron acceptors. Electrophiles react by accepting electrons into their LUMO, and better electrophiles have lower-energy LUMOs.

Example:
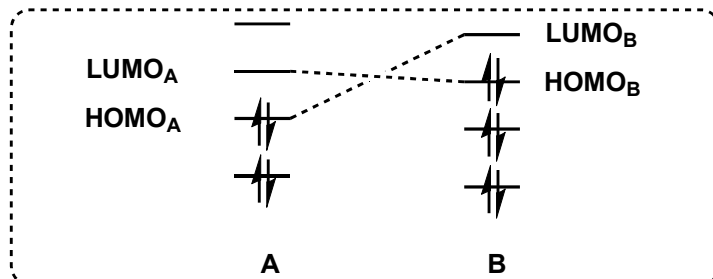
- The HOMO-LUMO gap (ΔE) is smaller when we consider the interaction between $HOMO_B$-$LUMO_A$.
- B will be the nucleophile and A will be the electrophile.

Workshop Problems

Workshop Problem 1: Hybridization and p-System Orbitals

For each of the following molecules: (i) indicate the hybridization on each non-hydrogen atom and draw in any missing lone pairs and (ii) provide a clear, three-dimensional drawing of the p-orbitals that make up the π-system on each molecule.

1-a.

1-b.

1-c.

1-d. $H_2C=C=CH_2$
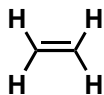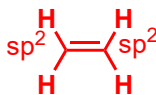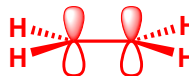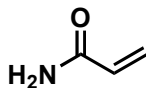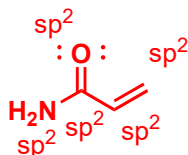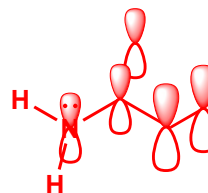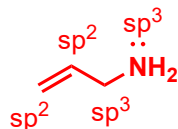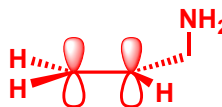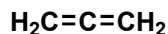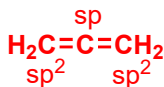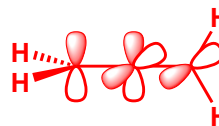
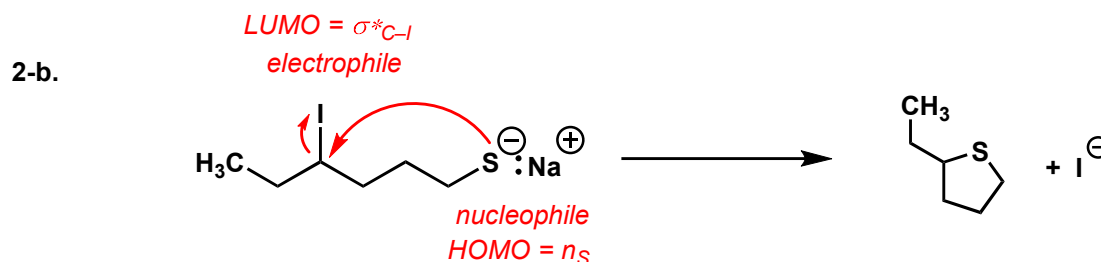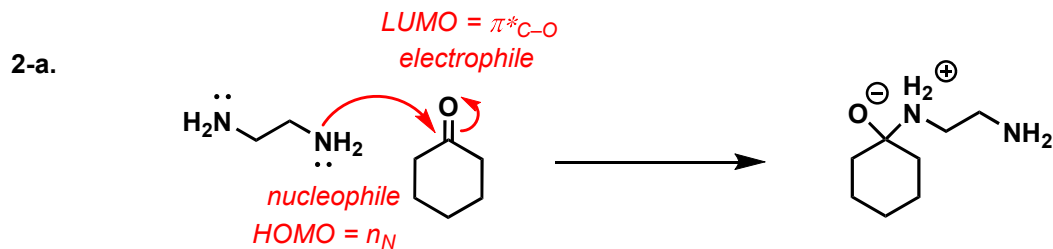**Workshop Problem 2: Nucleophiles and Electrophiles**

For each reaction, identify and label the reactive HOMO and LUMO. Identify the nucleophile and electrophile in each reaction and provide arrow-pushing mechanisms.
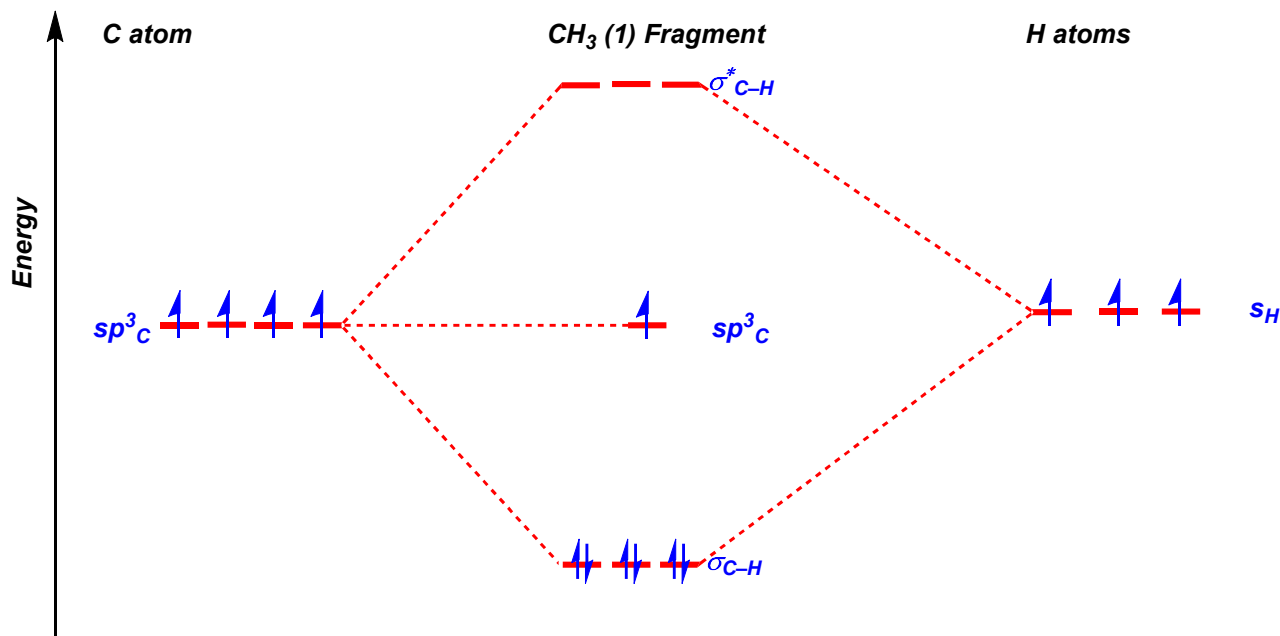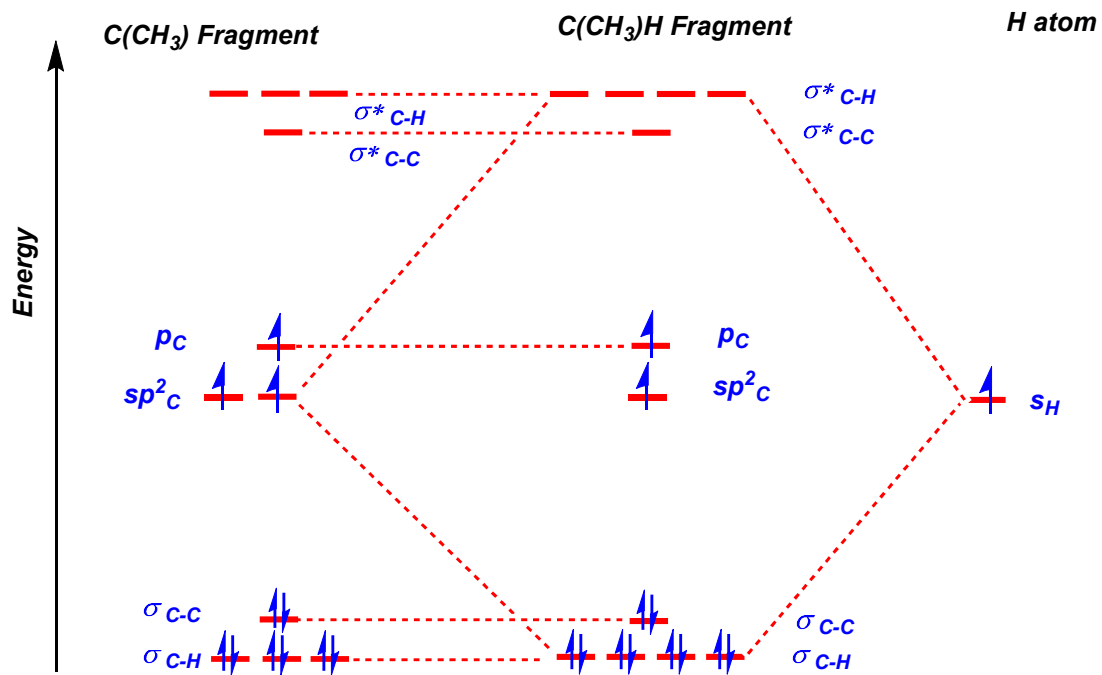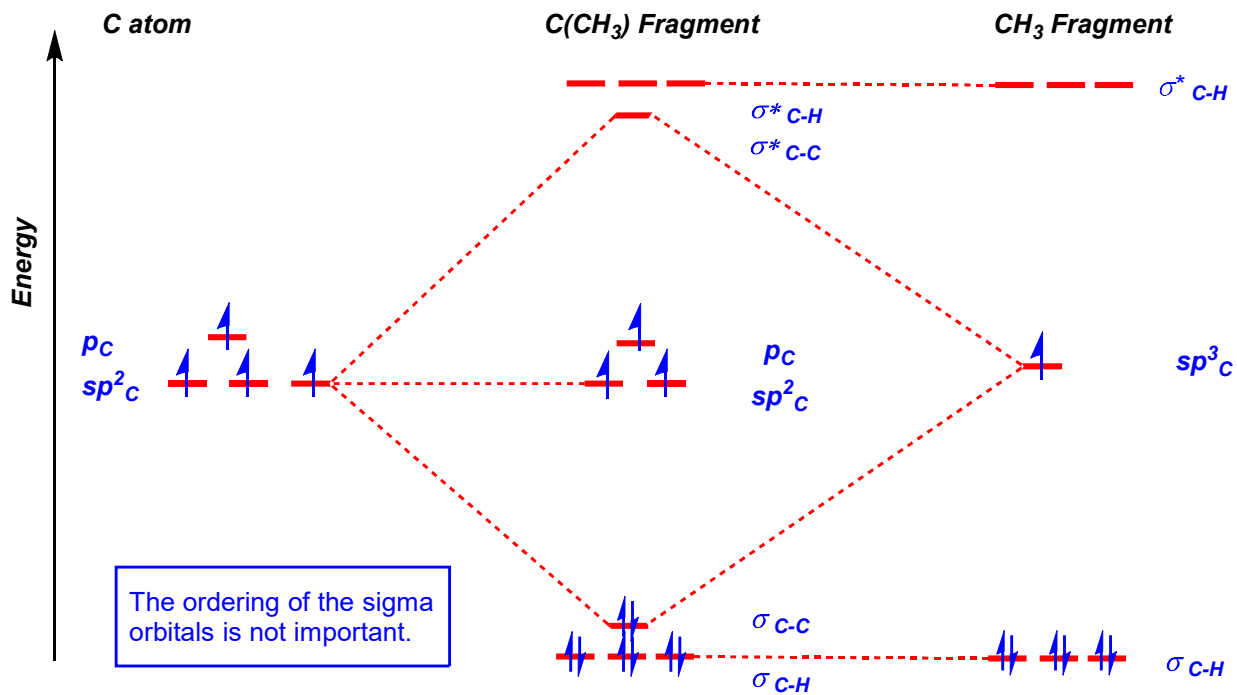
2-a.

LUMO = π^*_{C-O}
electrophile

H_2N ⁀ NH_2 O (cyclohexanone) → O⁻ $\overset{\oplus}{\underset{H_2}{N}}$ ⁀ NH_2

nucleophile
HOMO = n_N

2-b.

LUMO = σ^*_{C-I}
electrophile

H_3C ⁀ (chain with I) ⁀ $\overset{\ominus}{S} \overset{\oplus}{:Na}$ → CH_3 (thiolane ring) $+ I^{\ominus}$

nucleophile
HOMO = n_S

Workshop Problem 3: In this class we will discuss many reactions that focus on the reactivity of carbonyls. Let's explore this using frontier molecular orbital theory.
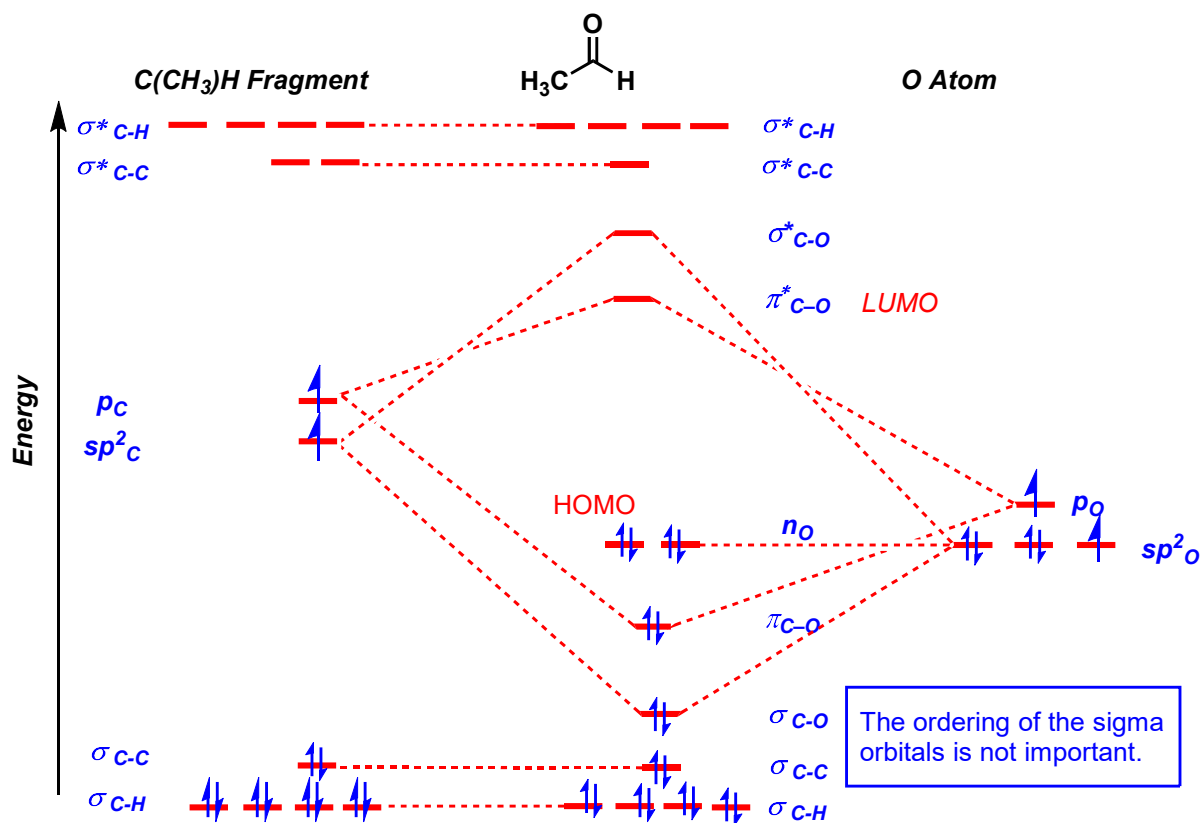
3a. Based on the structures provided, draw curly arrows to depict the flow of electrons for the reaction mechanism. Identify and label the HOMO and LUMO

1 H_3C $\overset{O}{\underset{2}{C}}$ H $\overset{\ominus}{O}H$ ⇌ H_3C $\overset{O^{\ominus}}{\underset{H}{C}}$ OH
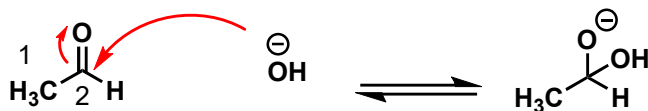
3b. Now we are going to justify why the molecules reacted the way they did by constructing an MO diagram of acetaldehyde using the fragment method. Remember to think about the hybridization of different atoms!

Energy

C atom   CH₃ (1) Fragment   H atoms

σ^*_{C-H}

sp^3_C sp^3_C s_H

σ_{C-H}

Top diagram:

C atom — C(CH₃) Fragment — CH₃ Fragment

σ^*_{C-H}
σ^*_{C-C}

p_C
sp^2_C

p_C
sp^2_C

sp^3_C

The ordering of the sigma orbitals is not important.

σ_{C-C}
σ_{C-H}

σ_{C-H}

Bottom diagram:

C(CH₃) Fragment — C(CH₃)H Fragment — H atom

σ^*_{C-H}
σ^*_{C-C}

σ^*_{C-H}
σ^*_{C-C}

p_C
sp^2_C

p_C
sp^2_C

s_H

σ_{C-C}
σ_{C-H}

σ_{C-C}
σ_{C-H}

ii) Now take your final MO of your reactant and place the MOs for OH in the corresponding energy levels

iii. Finally, label the energy levels corresponding to the HOMO and LUMO for both acetaldehyde and hydroxide.
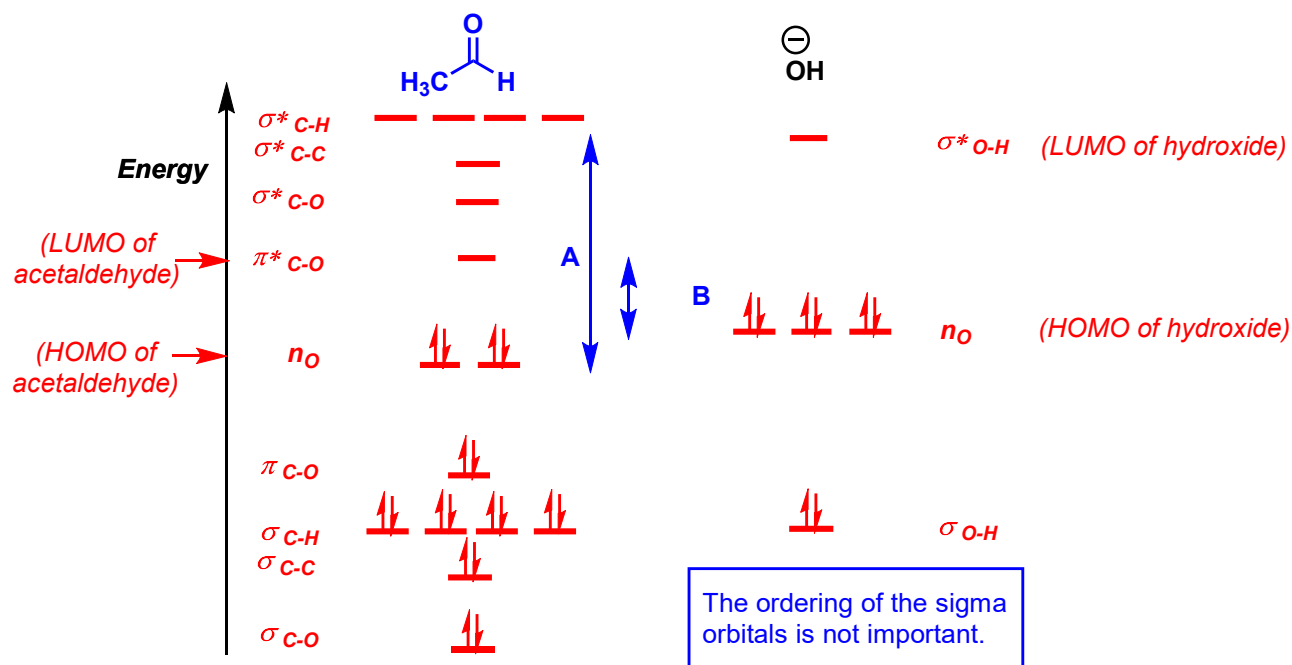
3-c. Identify the two possible HOMO/LUMO interactions. Determine which interaction seems more plausible, and provide a rationale for your decision.

The two possible interactions are **A)** n_O (acetaldehyde) $+ \sigma^*_{O-H}$ (hydroxide) and **B)** n_O (hydroxide) $+ \pi^*_{C-O}$ (acetaldehyde). The HOMOs of acetaldehyde and hydroxide are both non-bonding and have similar energy levels (the HOMO of hydroxide is actually higher because of the negative charge makes the oxygen atom effectively less electronegative). However the LUMO of acetaldehyde (π^*_{C-O}) is significantly lower in energy than the LUMO of hydroxide (σ^*_{O-H}). This results in a smaller energy gap between the n_O (hydroxide) $+ \pi^*_{C-O}$ (acetaldehyde) HOMO/LUMO pair (**B < A**), making this interaction more favorable.

Practice Problems

Skillbuilder Problem 1: Hybridization and p-System Orbitals

For each of the following molecules: (i) indicate the hybridization on each non-hydrogen atom and draw in any missing lone pairs and (ii) provide a clear, three-dimensional drawing of the p-orbitals that make up the π-system on each molecule.
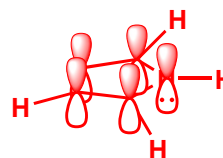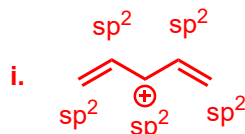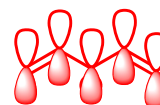
1-a.   HCN
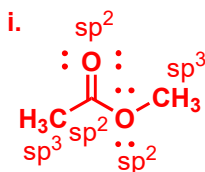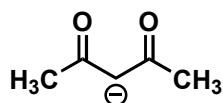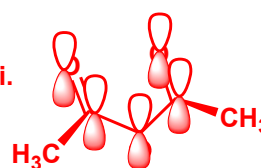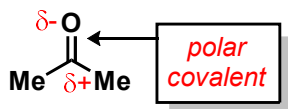

1-b.
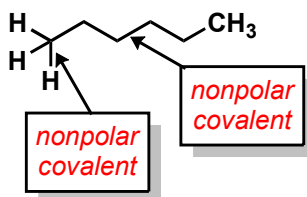

1-c.

1-d.

1-e.
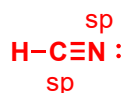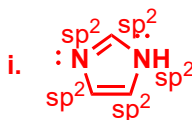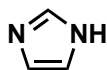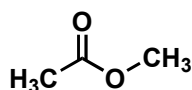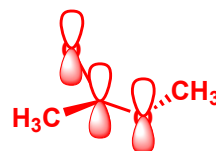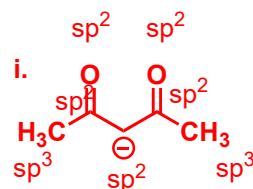
Skillbuilder Problem 2: Polar Bonds

Label each of the indicated bonds as "ionic", "polar covalent " or "nonpolar covalent". Indicate all of the full and/or partial charges on each compound.
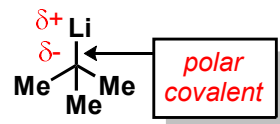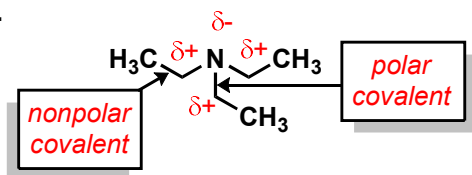
2-a.

polar covalent

2-b.

nonpolar covalent

nonpolar covalent

2-c.

polar covalent

2-d.

nonpolar covalent

polar covalent

2-e.

ionic

polar covalent
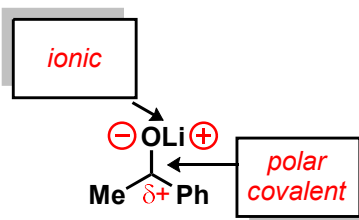
Skillbuilder Problem 3: Nucleophiles and Electrophiles
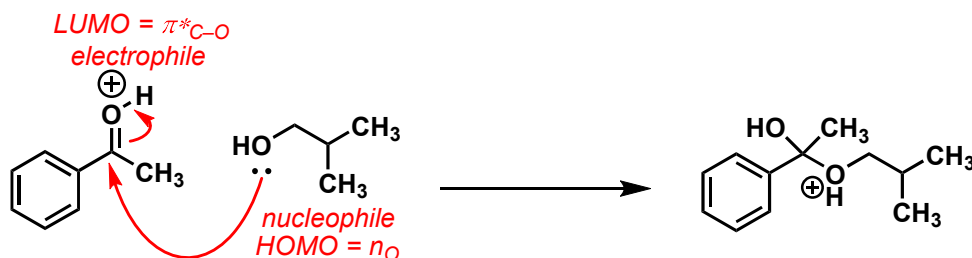
For each reaction, identify and label the reactive HOMO and LUMO. Identify the nucleophile and electrophile in each reaction and provide arrow-pushing mechanisms.
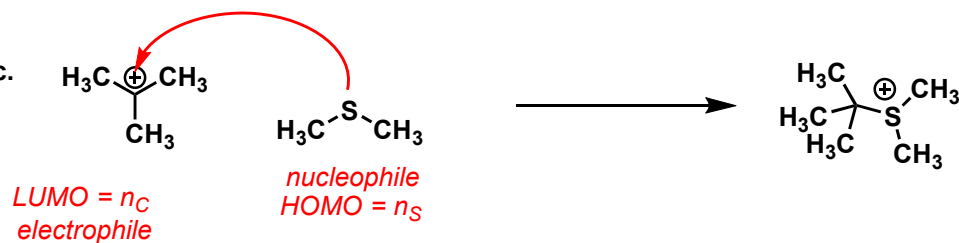
3-a.

nucleophile
HOMO = n_O

electrophile
LUMO = σ^*_{C-Br}

3-b.

LUMO = π^*_{C-O}
electrophile

nucleophile
HOMO = n_O

3-c.

LUMO = n_C
electrophile

nucleophile
HOMO = n_S
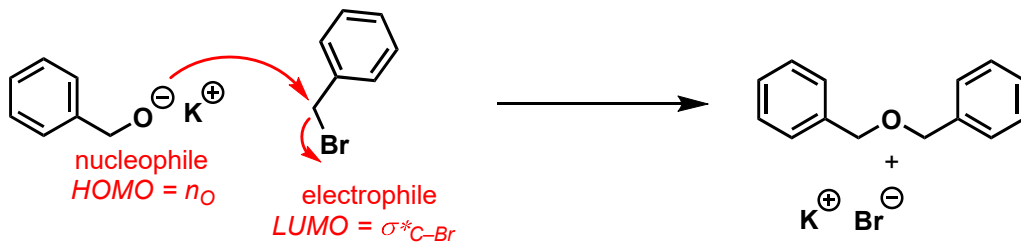
Challenge problems represent a higher level of difficulty than skillbuilder problems, typical of that found on midterm exams. You may need to integrate several concepts and apply them in order to answer the question.

Challenge Problem 1

1-a. Provide Lewis dot structures for the isoelectronic species, ^-CN and CO below. Include all lone pairs and formal charges, and indicate the hybridization of each atom.

$$sp \; : C^{\ominus} \! \equiv \! N : \; sp \qquad\qquad sp \; : C^{\ominus} \! \equiv \! O^{\oplus} \; sp$$

4-b. Complete the molecular orbital (MO) diagrams for ^-CN and CO by adding the remaining accurately-placed atomic and molecular orbitals on the same relative energy scale. Label each atomic and molecular orbital energy level, and fill in the proper number of electrons (in the molecular orbitals only).
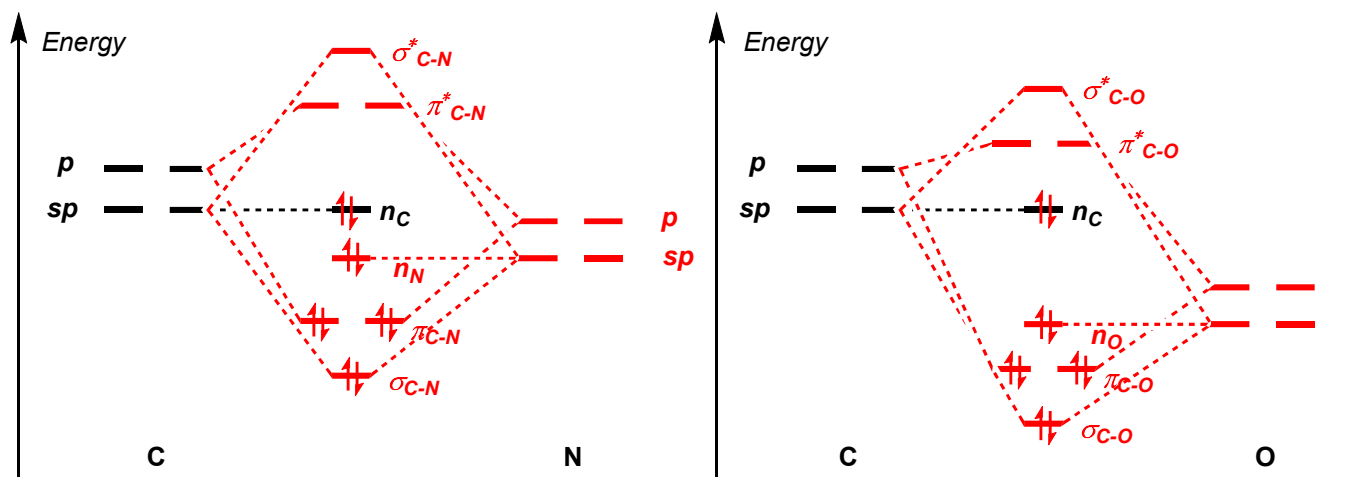
4-c. Using the MOs from your diagram as a guide, draw the $\sigma_{C\text{-}N}$ molecular orbital of ^-CN and the $\sigma_{C\text{-}O}$ molecular orbital of CO.

$\sigma_{C\text{-}N}$ *(sigma bond)* $\sigma_{C\text{-}N}$ *(sigma bond)* $\sigma_{C\text{-}O}$ *(sigma bond)* $\sigma_{C\text{-}O}$ *(sigma bond)*

4-d. Using the MOs from your diagram as a guide, draw the non-bonding molecular orbitals of ^-CN and CO.

lone pair in n_C   *lone pair in n_N*   *lone pair in n_C*   *lone pair in n_O*

4-e. Using the MOs from your diagram as a guide, provide a clear, three-dimensional drawing of the p orbitals that make up the $\pi_{C\text{-}N}$ molecular orbitals of ^-CN. Do the same for CO.

*2 x $\pi_{C\text{-}N}$ (pi bonds)*   *2 x $\pi_{C\text{-}O}$ (pi bonds)*

4-f. Based on your analysis in part **b,** would you expect CO or CN- to have a stronger covalent component to its bond? Justify your answer.
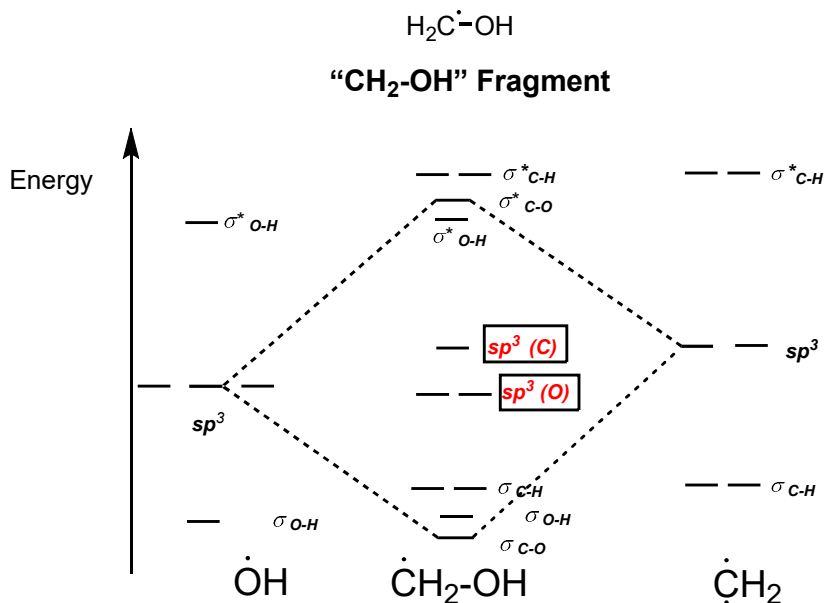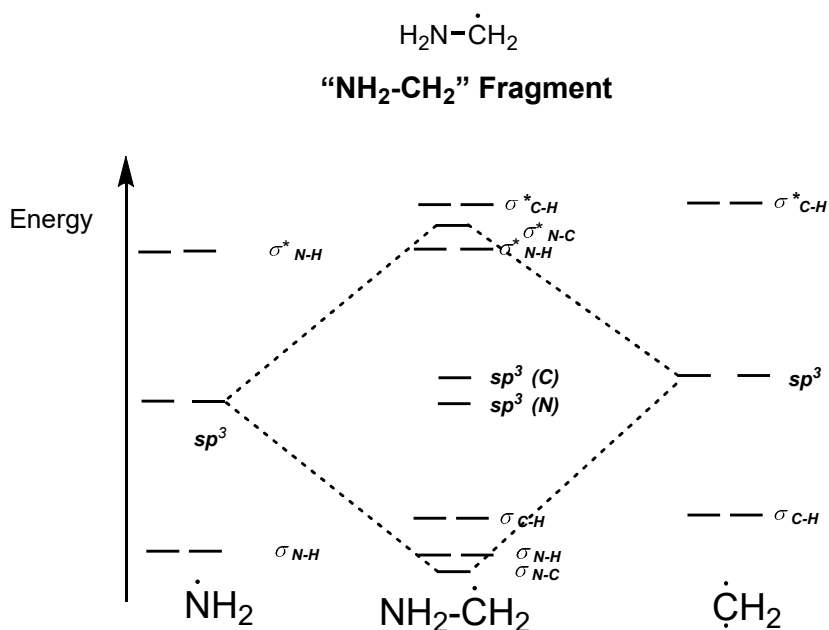
Covalent bonding character arises when orbitals are of the correct symmetry and energy to overlap. From the above MO diagram, we see that the symmetry of the orbitals is the same for both components, so the only difference in their bonding characters lies in the energetic differences. Since C and N have a smaller ΔEN than C and O, the orbitals are closer in energy and are thus able to mix better to form a covalent bond. Therefore, you would expect CN- to have a stronger covalent component in its bonding relative to CO.

Challenge Problem 2

2-a. A qualitative molecular orbital analysis of ethanolamine is helpful for predicting its reactivity as a nucleophile. Begin by labeling the hybridization of each non-hydrogen atom on the structure of ethanolamine.

sp^3 sp^3

H_2N⌒⌒OH

sp^3 sp^3
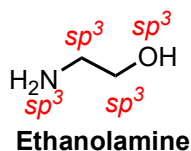
Ethanolamine

2-b. A molecular orbital diagram for ethanolamine can be constructed below by combining one "H_2N-CH_2" fragment and one "CH_2-OH" fragment. The diagrams for those two fragments are shown below. Label the unlabeled orbitals of the "CH_2-OH" fragment. You do not yet need place electrons on the diagrams.

$H_2N-\dot{C}H_2$

"NH₂-CH₂" Fragment

Energy

σ^*_{N-H}

σ^*_{C-H}
σ^*_{N-C}
σ^*_{N-H}

σ^*_{C-H}

sp^3 (C)
sp^3 (N)

sp^3

sp^3

σ_{C-H}
σ_{N-H}
σ_{N-C}

σ_{C-H}

σ_{N-H}

$\dot{N}H_2$ NH_2-$\dot{C}H_2$ $\dot{C}H_2$

$H_2\dot{C}-OH$

"CH₂-OH" Fragment

Energy

σ^*_{O-H}

σ^*_{C-H}
σ^*_{C-O}
σ^*_{O-H}

σ^*_{C-H}

sp^3 (C)
sp^3 (O)

sp^3

sp^3

σ_{C-H}
σ_{O-H}
σ_{C-O}

σ_{C-H}

σ_{O-H}

$\dot{O}H$ $\dot{C}H_2$-OH $\dot{C}H_2$

2-c. The MO diagram for ethanolamine is constructed below by combining the two fragments from part (b). Place the orbitals that you labelled in (b) on the "CH$_2$OH" fragment below at the correct energies relative to the "NH$_2$CH$_2$" orbitals. Then, draw and label the missing MOs of ethanolamine (hint: all the σ and σ* MOs of ethanolamine have already been drawn for you). Fill your MO diagram with the appropriate number of electrons. Label the HOMO in the final MO diagram for ethanolamine.

NH$_2$-ĊH$_2$ **Ethanolamine**   ĊH$_2$-OH
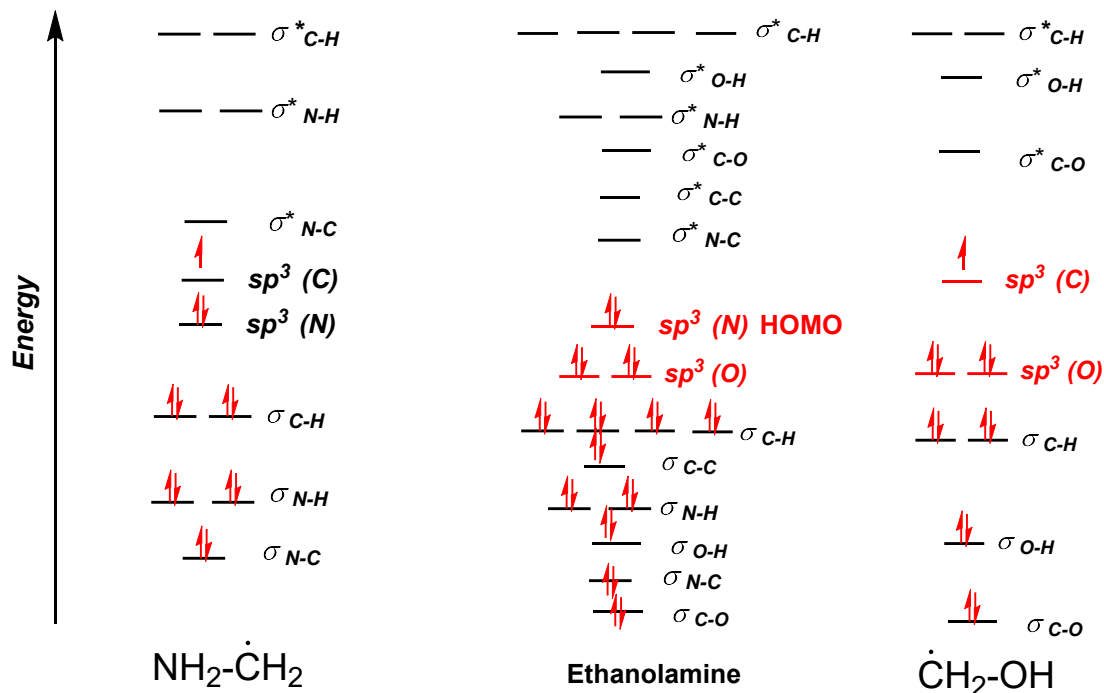
2-d. Ethanolamine can react reversibly with acetone. Identify the key orbitals (i.e. the HOMO and the LUMO) for the two possible reactions between ethanolamine and acetone displayed below in A and B. For each possible reaction, provide a mechanism using the curved arrow formalism. In the space below, draw and label the orbitals involved in each reaction. Which would you expect to form more rapidly? Justify your answer using FMO arguments based on your MO diagram in 2-c (2-3 sentences).

A:

B:

A:

n$_N$ -> π*$_{CO}$

B:

n$_O$ -> π*$_{CO}$
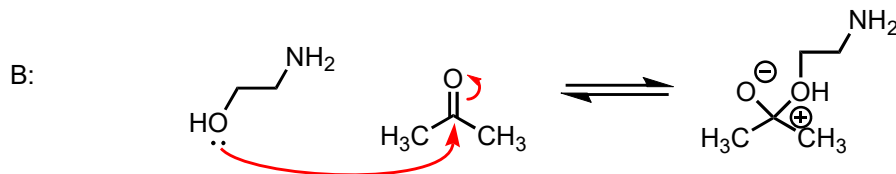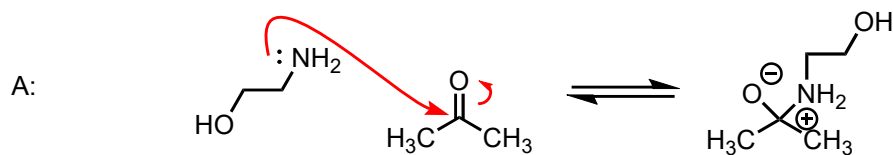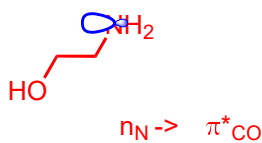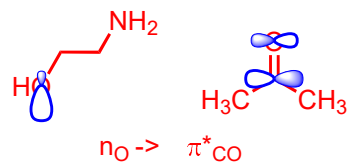
We would expect to form the product in reaction A more rapidly since the non-bonding nitrogen orbital is higher in energy than the non-bonding oxygen orbital due to the electronegativity difference. Thus, the energy difference between the HOMO and LUMO of A would be smaller. That is, nitrogen is more nucleophilic.